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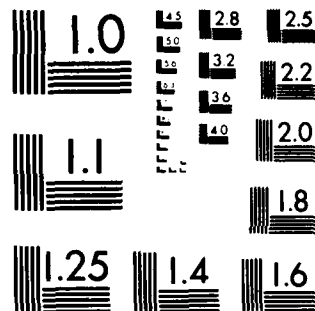
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Theoretical Studies of Kinetic
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Formation in Plasmas

Final Technical Report



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Theoretical Studies of Kinetic
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Formation in Plasmas

Final Technical Report

Contract No. F49620-81-C-0022
Project Task 2301/A7

REPORTED BY

H. H. Michels

R. H. Hobbs

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APPROVED BY

G. A. Peterson

DATE March 1983

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	CH_3^-	
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<p>This technical program constitutes a theoretical research investigation of the kinetic mechanisms of negative ion formation in plasmas. This study was directed toward elucidating the mechanisms of the most important volume-dependent reactions that occur in hydrogen-ion H^- (D^-) source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type. The primary goal of this research program was to identify the most important reactions leading to H^- (D^-) production or destruction and to estimate these reaction rates as a function</p>		

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of system parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies.

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FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Corporation, Research Center, East Hartford, Connecticut, under Contract F49620-81-C-0022, Project-Task No. 2301/A7. The performance period for the technical program was from 15 January 1981 through 15 January 1983. The project monitors were Lt. Colonel Anthony K. Hyder, Jr., and Captain Henry L. Pugh, Jr., USAF.



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Theoretical Studies of Kinetic Mechanisms
of Negative Ion Formation in Plasmas

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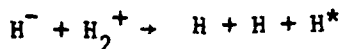
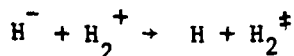
ABSTRACT

This technical program constitutes a theoretical research investigation of the kinetic mechanisms of negative ion formation in plasmas. This study was directed toward elucidating the mechanisms of the most important volume-dependent reactions that occur in hydrogen-ion, $H^+(D^+)$, source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type. The primary goal of this research program was to identify the most important reactions leading to $H^+(D^+)$ production or destruction and to estimate these reaction rates as a function of system parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies.

STATEMENT OF WORK

The Contractor shall conduct a theoretical research investigation of the electronic structure of negative molecular ions and the kinetic mechanisms of negative ion formation in plasmas. This investigation shall include the calculation of potential energy hypersurfaces for ion-atom and ion-molecule gas phase interactions that occur in magnetron-type negative ion source devices. In addition, calculations shall be performed to estimate the rates of the most important volume dependent reactions leading to H^- production or destruction in such devices. Experimental data collected from ongoing studies with negative ion source devices shall be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out with ab initio methods using electronic structure and kinetic cross-section codes that have previously been developed or modified at this Center. Specifically, this investigation shall comprise the following:

- (a) Quantum mechanical calculations of the potential energy hypersurfaces describing the following reactions:



- (b) Quantum mechanical calculations of the cross-sections and kinetic rates for the reactions specified in (a) above, including predictions of product states and branching ratios.
- (c) A survey of current experimental studies on negative ion source devices and comparisons of available gas phase kinetic data with the results obtained from this theoretical study.
- (d) Quantum mechanical calculations of the low-lying potential energy hypersurfaces for the CH_2/CH_2^- system. This study shall include an analysis of the reaction kinetic paths for production of H^- from photodissociation of CH_2^- or hydrocarbon systems which exhibit a similar chemistry.
- (e) Quantum mechanical calculations of the potential energy curves for Li_2/Li_2^- and an analysis of the probability of Li^- formation via dissociative-attachment of $e + Li_2^+$.

Other gas phase reactions, than those specified in (a) above, may be substituted for detailed study if experimental and particle beam program directions indicate more optimum choices. Items (a), (b), and (c) were tasks that were scheduled for CY81. Items (d) and (e) were tasks scheduled for CY82.

BACKGROUND

Recent successes in the tokamak program and in other controlled thermonuclear research programs (Ref. 1) have focused attention on the problem of developing an efficient high-energy particle beam source. For several applications, a neutral beam with energies above 200 keV is desired. The acceleration of negative ions (primarily H^- or D^-) to such energies, followed by neutralization through a stripping reaction, appears at the present time to be the most efficient approach for producing a high energy neutral particle beam.

In another area, the feasibility of particle beams (both charged and neutral) as military weapons has been under study. The proposed endoatmospheric applications require high intensity sources and mainly focus on the problems of beam stability and propagation characteristics. Exoatmospheric applications require lower intensity sources but of very high quality. Design goals are highly collimated beams with a narrow energy spread.

A magnetron-type negative H^- source has been reported by Belchenko, Dimov and Dudnikov (BDD) (Ref. 2) that has produced H^- current densities of several $A\ cm^{-2}$. This device operates as a plasma discharge in an atmosphere of hydrogen gas with cesium or other alkalis present at ~ 0.1 percent. The mechanism for the production of H^- is believed to involve a catalyzed surface reaction whereby H^- ions are produced by transfer of electrons from Cs atoms that are adsorbed on the cathode surface (Refs. 3, 4). The detailed kinetic mechanisms of such surface reactions are still uncertain and parametric experimental studies are currently underway at LASL, LBL, IRT and at other laboratories to elucidate the mechanisms and operating characteristics of BDD and similar devices and to develop information for their scale-up to higher current densities. Diagnostics of H^- source devices are also underway at Brookhaven (Ref. 5) using beam probe and spectroscopic techniques.

Concurrent with these surface-plasma reactions are several electron-H volume-dependent processes that may lead either to the production of H^- or, in reverse, may act as important destructive processes of the negative ions after they are formed. Photodetachment experiments by Bacal and Hamilton (Ref. 6) in hydrogen plasmas indicate H^- densities 100 times larger than that predicted from simple electron attachment mechanisms. Further, these experiments indicate a nonlinear dependence of the production of H^- on electron density, at least for densities less than $10^{10}\ cm^{-3}$. Several mechanisms (Ref. 7) have been proposed to explain these volume-dependent H^- production processes but the cross-sections for many of the reactions leading to H^- are uncertain.

By a large margin, the major thrust of the development of particle beam technology has been experimental in nature. Theoretical studies of surface catalyzed reactions leading to H^- production have been undertaken by LLL (Ref.

4), but only a relatively small theoretical effort (Ref. 8) has been directed toward detailed calculations of cross-sections for volume-dependent reactions. Because of the difficulty of conducting experiments to measure these unknown cross-sections, the development of a sound theoretical method for calculating these state-to-state processes appeared desirable. Although relatively little work of this nature has been done in the past, enough theoretical work is available to indicate that the development of such procedures can be made practical, particularly if good wave functions and potential energy surfaces are available for the interacting species.

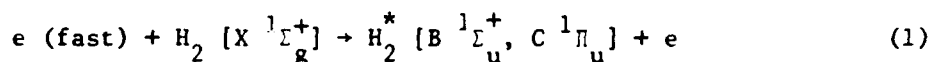
The original goal of this technical program was to delineate the most important volume dependent reactions that lead to $H^-(D^-)$ production (or destruction) and to calculate the energetics and cross-sections of such reactions as a function of system parameters. Attention was also directed toward those kinetic processes that are of importance in high pressure ion source devices, particularly of the BDD type. It was intended that this theoretical program should compliment experimental studies with negative ion source devices. A cooperative program of ongoing experimental research and our theoretical studies are of mutual benefit and result in a better understanding of the fundamental physical processes occurring in ion source devices.

A further goal of this research program was to explore new chemical sources for the production of light negative atomic ions, in particular H^- and Li^- . Studies included the formation of H^- or D^- via photodissociation of unsaturated hydrocarbon negative ions and the formation of Li^- via dissociative-attachment of electrons to molecular Li_2 .

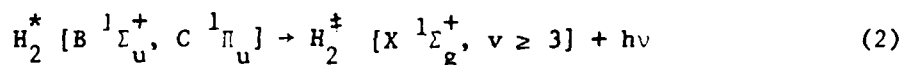
RESEARCH PROGRESS

In contrast to surface catalyzed reactions, the mechanisms of most of the known volume-dependent gas phase reactions involving H^- are relatively simple to analyze, although much remains to be done identify the state distributions for the products. A major problem, which has been addressed during the past year, has been to identify the most likely reaction kinetics leading to the formation of H^- atoms.

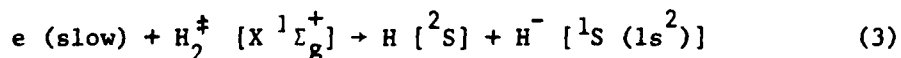
Hiskes (Ref.10) has proposed a mechanism for the production of vibrationally excited H_2 and the subsequent production of H^- via dissociative-attachment of electrons. The initial step proposed by Hiskes involves electron excitation of ground state H_2 to an electronically excited state:



Both of these states have allowed radiative transitions to the ground state of H_2 but the displaced equilibrium separations of these excited states yield vibrationally excited H_2 upon radiative decay according to the most favorable Franck-Condon transitions:

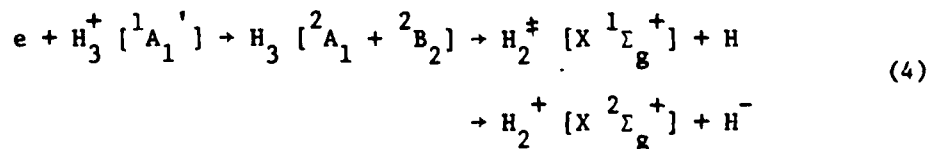


Vibrationally excited H_2 has been shown (Refs. 8, 9) to have a greatly enhanced cross-section for electron dissociative-attachment:

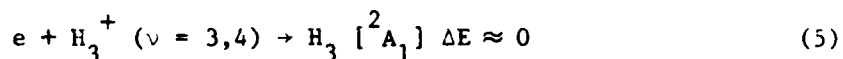


This proposed mechanism is critically dependent on the magnitude of the overall cross-section for reactions (1) and (2). Hiskes (Ref. 10) has estimated this cross section to be $\sim 10^{-18} \text{ cm}^2$, a rather low value for a volume-dependent route for the production of H^- .

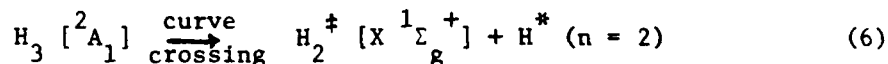
As an alternative mechanism for producing vibrationally excited H_2 , we have undertaken an analysis of the branching and product distribution for dissociative-recombination of $e + H_3^+$. The reaction scheme is as follows:



Detailed quantum mechanical calculations of these reaction surfaces have been carried out. The H_3 correlation diagram and possible low-lying dissociative-recombination reaction paths are indicated in Figs. 1 and 2, respectively. Dissociative recombination of $e + H_3^+$, as shown in reaction (4), is exothermic by 9.3 eV to form $H_2 + H$ and endothermic by 5.4 eV to form the ion pair, $H_2^+ + H^-$. However, the detailed branching of reaction (4) depends critically on the shape of the 2A_1 and 2B_2 hypersurfaces for H_3 for interatomic separations in the vicinity of 2-3 Å since the coulomb attraction of the ion pair gives rise to a degeneracy in the hypersurfaces of H_3 in this region. During the past year, we have undertaken a series of ab initio calculations of the potential energy surfaces for H_3 in both C_{2v} and $D_{\infty h}$ symmetries to ascertain the character of the low-lying states. These calculations were carried out using optimized Slater-type orbital (STO) basis functions and a full CI within each symmetry group. The resultant potential energy surfaces are shown in Fig. 3. Based on these results, we find a reaction path for dissociative recombination which involves the electron attachment of $e + H_3^+$ to form a symmetric 2A_1 state of H_3 which is nearly energy resonant for recombination of H_3^+ ions with three or four quanta of vibrational energy:

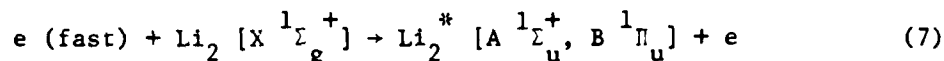


This state of H_3 correlates diabatically with the ion pair, $H_2^+ + H^-$, but exhibits many curve-crossings of the lower-lying Rydberg states of H_3 . In particular, the lowest-lying recombination pathway yields vibrationally excited H_2 molecules and electronically excited H with $n = 2$:

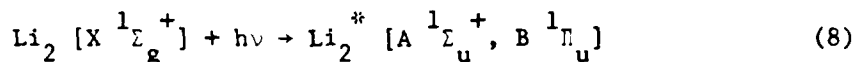


The overall recombination pathway is illustrated in Fig. 4. We find that the overall cross-section for this route to H_2^+ is $10^{-15} - 10^{-14} \text{ cm}^2$, and thus the rate of reaction (3) alone becomes rate determining. This study indicates that dissociative-recombination is a kinetically important volume dependent reaction for production of vibrationally excited H_2 in high density hydrogen plasmas and may be a significant factor as a source of H^- in high density plasma devices.

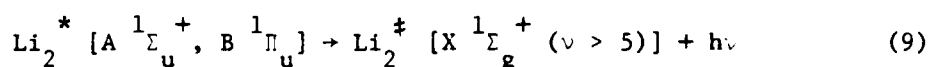
In addition to these studies of dissociative-recombination of $e + H_3^+$, we have undertaken a series of calculations of Li_2^- in order to access the energetics of this anion. McGeoch (Ref. 11) has suggested that a Li^- source should be possible through a series of reactions similar to those found for H_2 . The initial step involves the formation of the Li_2 dimer and excitation to low-lying excited states via fast electron collisions or photon pumping. The latter process is that currently being investigated by McGeoch. The reactions are:



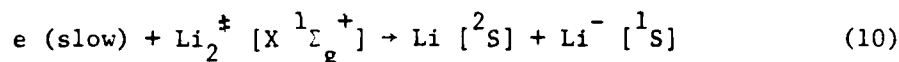
or



The $A \ ^1\Sigma_u^+$ and $B \ ^1\Pi_u$ state both exhibit fast radiative decay back to the ground $X \ ^1\Sigma_g^+$ state but the most favorable Franck-Condon transitions favor population of Li_2 with $v = 5$ or greater:



Our present understanding of the energetics of the $\text{Li}_2/\text{Li}_2^-$ system are shown in Fig. 5. The dashed curves were estimates based on H_2^- and the known molecular orbital structure of Li_2^- . Our most recent ab initio calculations, however, indicate that the lowest $^2\Sigma_g^+$ state of Li_2^- , is slightly attractive all the way in to the curve-crossing with the ground state of Li_2 . This suggests that electron dissociative-attachment is possible for this system for vibrationally excited Li_2 molecules:



The potential energy curves governing reaction (10) are shown in Fig. 5. There is still considerable uncertainty in the location of the excited states of Li_2^- , especially in the auto-ionizing region above $\text{Li}_2 + e$. The ground $[X \ ^2\Sigma_g^+]$ state is well characterized theoretically (Refs. 12, 13)² but little is known about the location of the low-lying excited electronic states which connect to $\text{Li} [^2P] + \text{Li}^- [^1S]$. In addition, by analogy with H_2^- , low-lying electronic states of Li_2^- with MO configuration $(1\sigma_g^2 1\sigma_u^2 2\sigma_g 1\pi_u^2) [^2,4\Sigma_g^+]$ may, in fact, actually lie lower than some of the states shown in Fig. 5. Such states dissociate to very high atom-ion limits and their general characteristics are uncertain. The curves shown in Fig. 5 represent our best estimates at the present time but more definitive calculations are required to define the curve-crossing regions for dissociative-attachment.

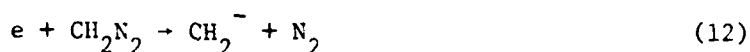
The lowest $^2\Sigma_g^+$ state of Li_2^- has the molecular orbital configuration $[1\sigma_g^2 1\sigma_u^2 2\sigma_g 2\sigma_g]$ for large separations and was the focus of our studies of this system during the past year. At short internuclear separations, this state mixes with a second bound $^2\Sigma_g^+$ state arising from $\text{Li} [^2P] + \text{Li}^- [^1S]$ with a molecular orbital configuration $[1\sigma_g^2 1\sigma_u^2 2\sigma_g 2\sigma_g]$. This mixing at intermediate separations results in a lowering of the interaction potential for the lowest $^2\Sigma_g^+$ state. Our preliminary calculations, as shown in Fig. 5, indicate that this mixing is stronger

than expected from MO considerations and lowers the $^2\Sigma_g^+$ potential curve into a feasible region for dissociative-attachment to occur.

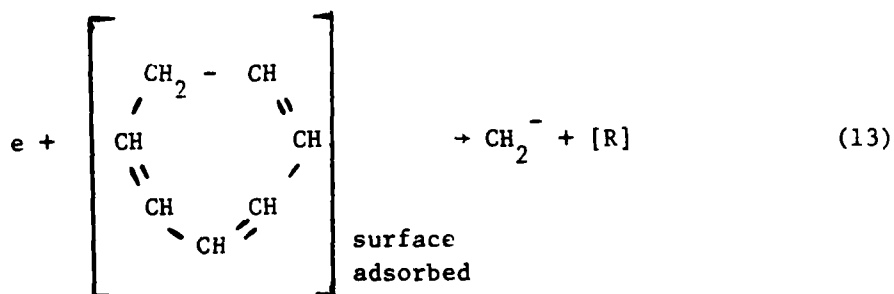
Further theoretical studies of these interaction potentials are required to define the overall reactive kinetics leading to Li^- production. A study parallel to that reported by Hiskes (Ref. 10) for H_2 should be carried out to estimate the overall cross sections for production of vibrationally excited Li_2^- . In addition, theoretical studies should be carried out to estimate the low-energy electron dissociative attachment cross-section for $e + \text{Li}_2^+ \rightarrow \text{Li} + \text{Li}^-$. The results of these studies would be of value to the experimental program of McGeoch (Ref. 11) to define the overall utility of this volume-dependent source of Li^- ions.

During the past year, our studies of novel H^- source reactions have included an analysis of the alkali hydride systems (LiH/LiH^-) and the energetics of the methylene anion. Several routes for producing the methylene anion have been investigated as experimental possibilities. These include:

- a) electron dissociative attachment of ethylene (C_2H_4) or diazomethane (CH_2N_2):

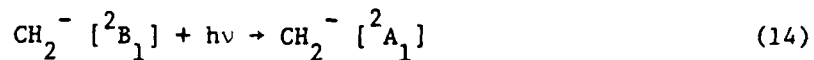


- b) electron attachment to surface adsorbed cycloheptatriene (C_7H_8):



where $[\text{R}]$ represents several possible hydrocarbon dissociation fragments.

The utility of these processes depends on the production of CH_2^- in the ground $^2\text{B}_1$ electronic state. Photon pumping of this state to the dissociating $^2\text{A}_1$ state is a possible route for H^- production:



Our calculations for the $\text{CH}_2/\text{CH}_2^-$ system are shown in Fig. 6. These studies indicate that the $^2\text{A}_1$ of CH_2^- is dissociative in the Franck-Condon region of the ground $^2\text{B}_1$ state but that a UV photon source would be required for optical pumping of this level. The attractiveness of this system is thus somewhat diminished but further studies of a similar nature for systems such as NH/NH^- may prove to be interesting.

Nine technical papers and presentations have resulted from the research efforts conducted under this contract.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals and Books

1. "Potential Energy Surface and Cross Sections for the $H^-(D^-) + H_2(D_2, HD)$ Ion-Molecule Reaction." H. H. Michels and J. F. Paulson, published as Chapter 22 in Potential Energy Surfaces and Dynamics Calculations, D. G. Truhlar, Ed., Plenum Press, New York, 1981, pp. 535-550.
2. "Spherical Harmonic Expansion Techniques for Multicenter Integrals Over STO's. A Re-examination for Vector Processing Computers." H. H. Michels, Published as a chapter in the Proceedings of the International Conference on ETO Multicenter Molecular Integrals, C. A. Weatherford, Ed., D. Reidel, Holland, 1982.
3. "Ab Initio Study of the Electronic Structure of Li_2^- ." H. H. Michels, R. H. Hobbs and L. A. Wright, to be published in Chemical Physics Letters, 1983.
4. "Dissociative-Recombination of $e + H_3^+$. An Analysis of Reaction Product Channels." H. H. Michels and R. H. Hobbs, to be published in Astrophysical Letters, 1983.

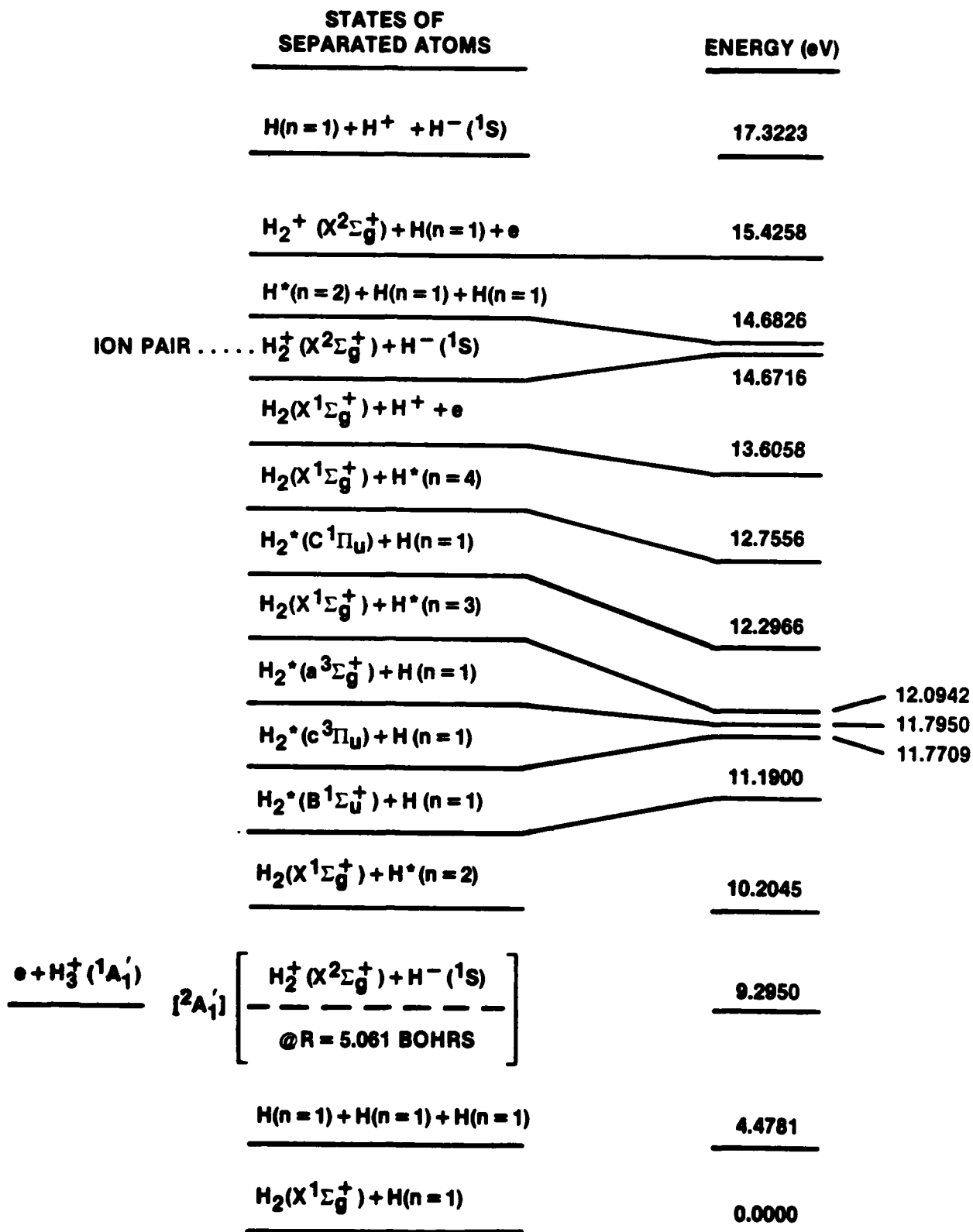
B. Technical Paper and Lecture Presentations

1. "Potential Energy Surfaces and Cross Sections for the $H^-(D^-) + H_2(D_2, HD)$ Ion-Molecule Reactions." Presented at the American Chemical Society Meeting, Las Vegas, Nevada, August 25-29, 1980.
2. "Spherical Harmonic Expansion Technique for Multicenter Integrals over STO's. A Re-examination for Vector Processing Computers." Presented at the International Conference on ETO Multicenter Molecular Integrals, Florida A&M University, Tallahassee, Florida, August 3-6, 1981.
3. "Volume Dependent Reactions for H^- and Li^- Production." H. H. Michels. Presented at the WHITE HORSE Ion Source Workshop, Los Alamos, NM, July 7-8, 1982.
4. "Dissociative-Recombination of $e + H_3^+$: An Analysis of Reaction Product Channels." H. H. Michels. Presented at the 35th GEC, Dallas, Texas, October 19-22, 1982.
5. "Dissociative-Recombination of $e + H_3^+$: An Analysis of Reaction Product Channels." H. H. Michels. Presented at the Sanibel International Symposium on Molecular Scattering Theory and Quantum Chemistry, Daytona Beach, Florida, March 2-7, 1983.

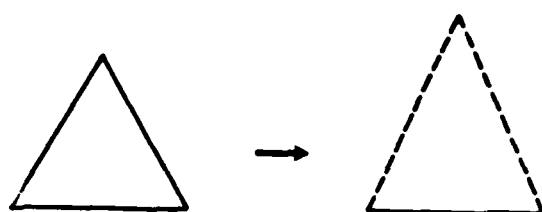
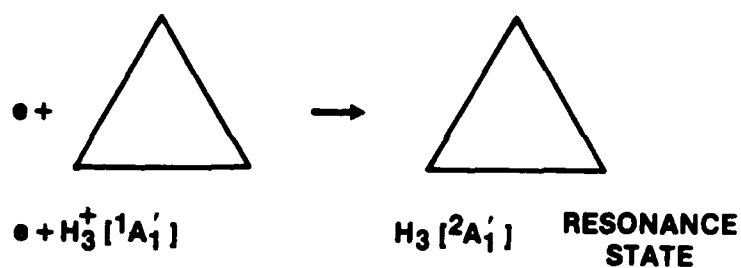
REFERENCES

1. Proceedings of the Eighth Symposium of Engineering Problems of Fusion Research. San Francisco, CA, November 1979.
2. Belchenko, Y. I., G. I. Dimov and V. G. Dudnikov: A Powerful Injector of Neutrals with a Surface-Plasma Source of Negative Ions. *Nuclear Fusion*, 14, p. 113, 1974.
3. Dimov, G. I.: Proceedings of the Second Symposium on Ion Sources and Formation of Ion Beams, Berkeley, CA, 1974.
4. Hiskes, J. R., A. Karo and M. Gardner: Mechanism for Negative-Ion Production in the Surface-Plasma Negative-Hydrogen-Ion Source. *Journal of Applied Physics*, 47, p. 3888, 1976.
5. Grossman, M. W.: H^- Ion Source Diagnostics. Proceedings of the Symposium on the Production and Neutralization of Negative Hydrogen Ions and Beams. Brookhaven National Laboratory, New York, 1977.
6. Bacal, M. and G. W. Hamilton: H^- and D^- Production in Plasmas. *Physics Review Letters*, 42, p. 1538, 1979.
7. Nicolopoulou, E., M. Bacal, and H. J. Doucet: Equilibrium Density of H^- in a Low Pressure Hydrogen Plasma. *Journal of Physics (France)*, 38, p. 1399, 1977.
8. Wadhera, J. M. and J. N. Bardsley: Vibrational- and Rotational-State Dependence of Dissociative Attachment in $e-H_2$ Collisions. *Physical Review Letters*, 41, p. 1795, 1978.
9. Allan, M. and S. F. Wong: Effect of Vibrational and Rotational Excitation on Dissociative Attachment in Hydrogen. *Physical Review Letters*, 41, p. 1791, 1978.
10. Hiskes, J. R.: Cross Sections for the Vibrational Excitation of the H_2 ($X^1\Sigma_g^+$) State via Electron Collisional Excitation of the Higher Singlet States. *Journal of Applied Physics*, 51, p. 4592, 1980.
11. McGeoch, M. W.: A Dissociative Attachment Li^- Source. AVCO/Everett Research Laboratory, work in progress.
12. Anderson, E. and J. Simons: A Calculation of the Electron Affinity of the Lithium Molecule. *Journal of Chemical Physics*, 64, p. 4548, 1976.
13. Dixon, D. A., J. L. Gole and K.¹D. Jordan: *Ab Initio* Study of the Electronic Structure of Li_2^- . *Journal of Chemical Physics*, 66, p. 567, 1977.

H₃ CORRELATION DIAGRAM

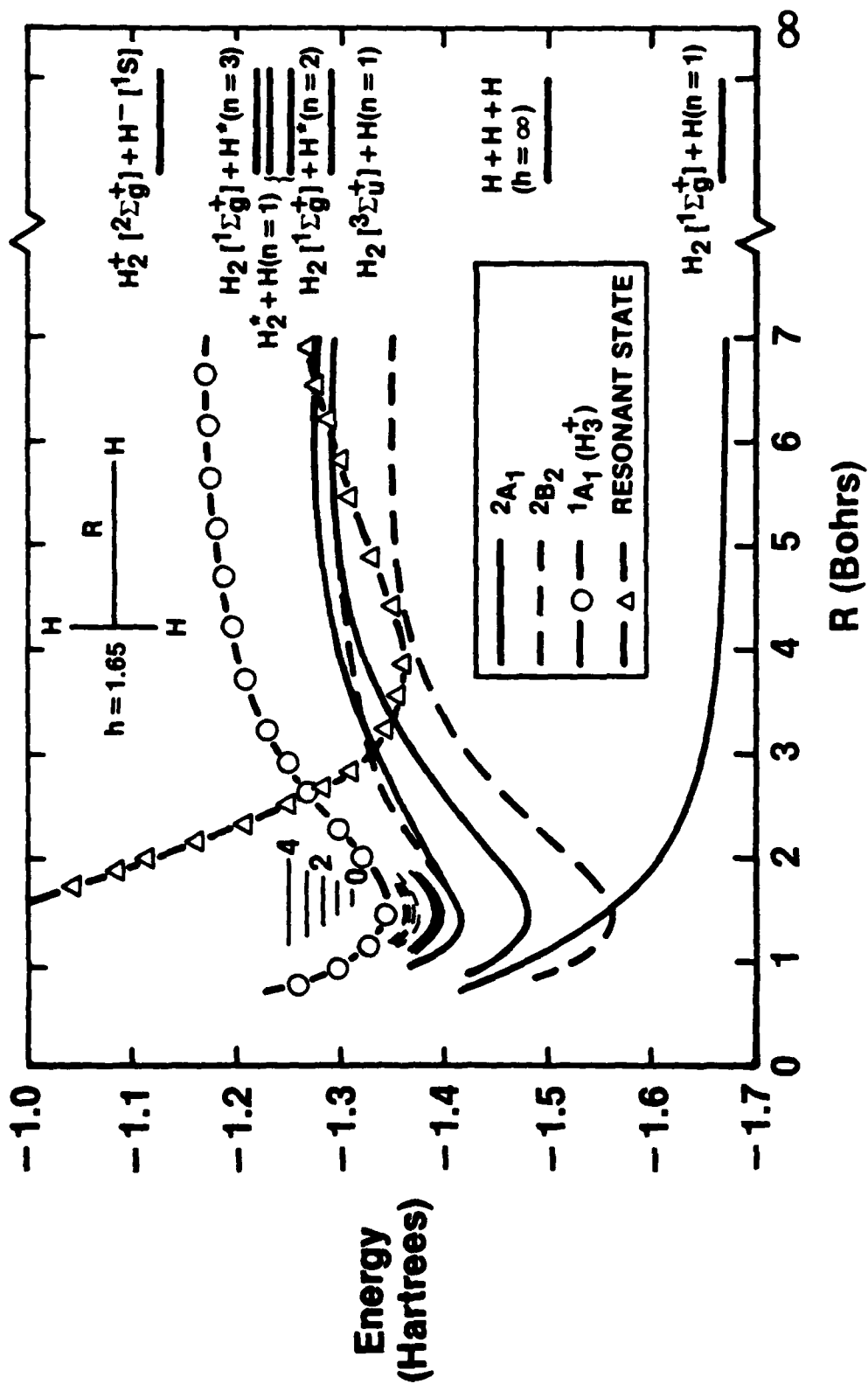


DISSOCIATIVE — RECOMBINATION REACTION PATHS



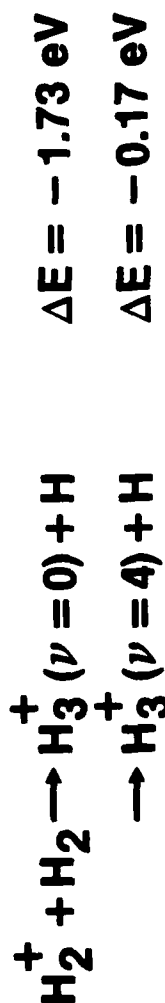
		<u>ΔE (eV)</u>
$\text{H}_3 [2A_1']$	$\rightarrow \text{H}_2 [X \ ^1\Sigma_g^+] + \text{H}^* (n=2)$	+ 0.91
	$\rightarrow \text{H}_2^* [B \ ^1\Sigma_u^+] + \text{H} (n=1)$	+ 1.89
	$\rightarrow \text{H}_2^* [c \ ^3\Pi_u] + \text{H} (n=1)$	+ 2.48
	$\rightarrow \text{H}_2^* [a \ ^3\Sigma_g^+] + \text{H} (n=1)$	+ 2.50
	$\rightarrow \text{H}_2 [X \ ^1\Sigma_g^+] + \text{H}^* (n=3)$	+ 2.80
	$\rightarrow \text{H}_2 [X \ ^1\Sigma_g^+] + \text{H}^+ + e$	+ 4.31
	$\rightarrow \text{H}_2^+ [X \ ^2\Sigma_g^+] + \text{H}^-$	+ 5.38

POTENTIAL ENERGY CURVES FOR H_3

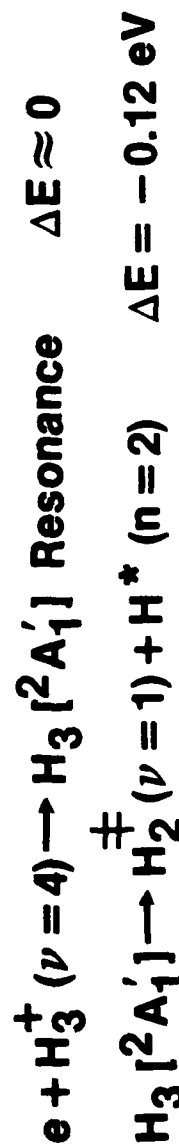


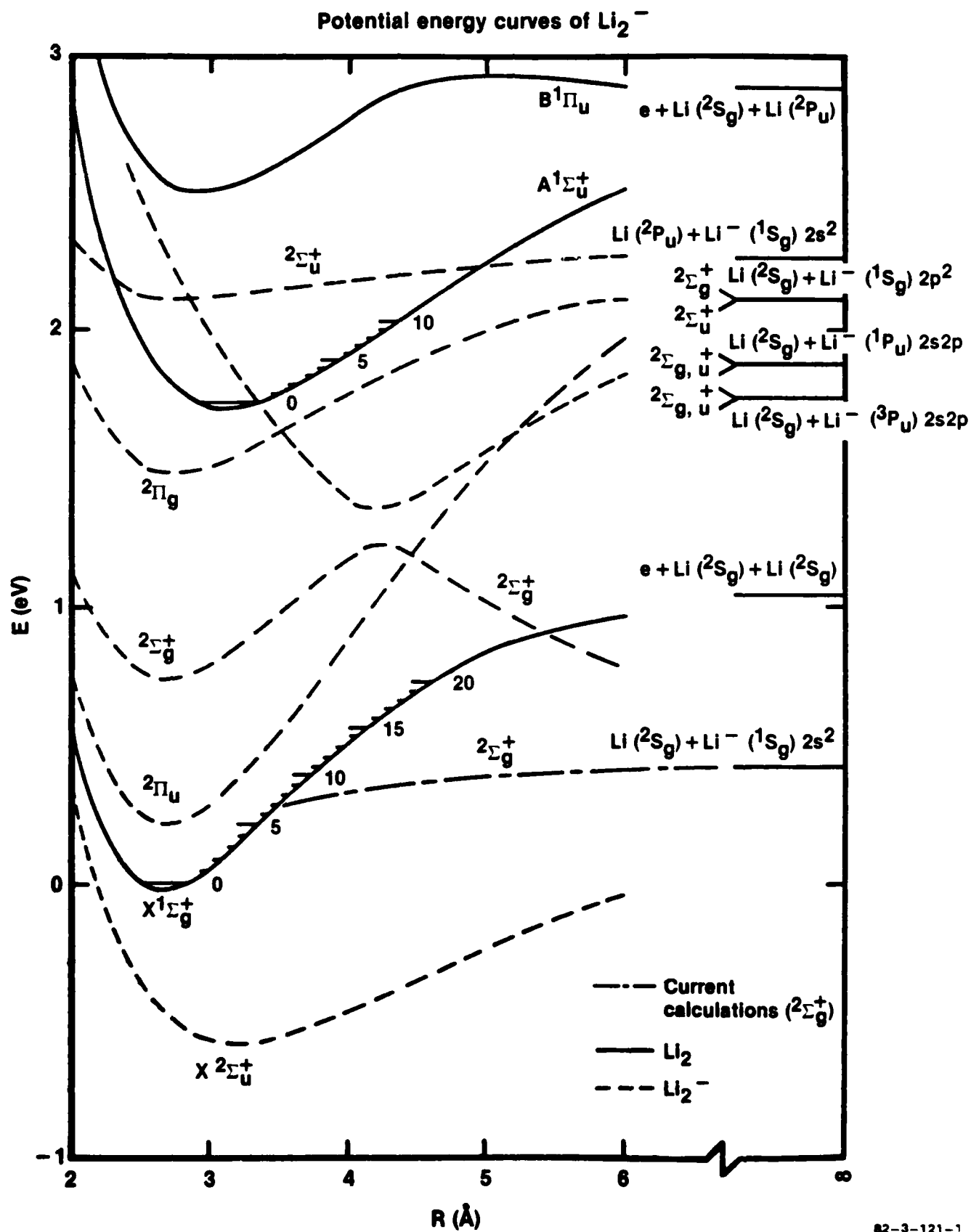
$e + H_3^+$ RECOMBINATION ENERGETICS

$e + H_3^+(\nu) \rightarrow H_3 \rightarrow H_2[X \ ^1\Sigma_g^+(\nu)] + H^*(n=2)$	ΔE (eV)
0	+0.91
1	+0.52
2	+0.13
3	-0.26
4	-0.64
4	-0.12



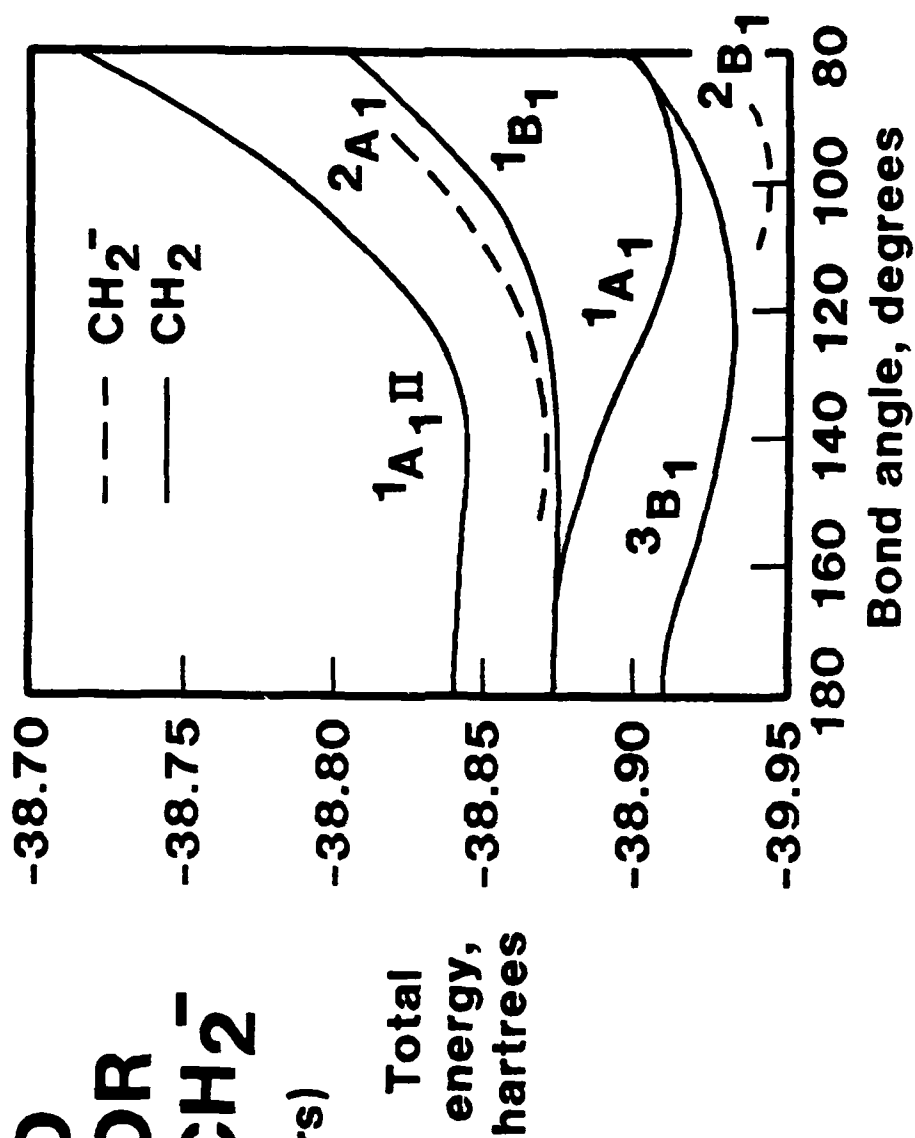
RECOMBINATION PATHWAY





82-3-121-1

TOTAL ENERGY VS BOND ANGLE FOR CH₂ AND CH₂⁻ (R = 2.10 Bohrs)



APPENDIX A

POTENTIAL ENERGY SURFACE AND CROSS SECTIONS
FOR THE $H^-(D^-) + H_2(D_2, HD)$ ION-MOLECULE REACTIONS*

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ABSTRACT

A uniform ab initio potential energy surface for the $H^- + H_2$ reaction has been constructed using an optimized double-zeta-plus-polarization-and-diffuse-orbital STO basis set within a configuration-interaction valence bond framework. Calculations have been carried out for both triangular and linear geometries to define the lowest singlet potential energy surface. From our energy contour diagrams we find the minimum energy reaction path corresponds to a linear conformation of $H^- + H_2$, in agreement with previous studies of this system. Our calculated barrier height is 15 kcal/mol, a value close to that obtained for the $H + H_2$ reaction using a similar quality basis set. The energy contours for $H^- + H_2$ for the isosceles triangle arrangement of the nuclei indicate that the least energy path leads to dissociation into $H^- + H + H$. Experimental cross sections have been measured for the $H^- + D_2(HD)$ and $D^- + H_2(HD)$ ion-exchange reactions in the energy range from 0.5 to 10.0 eV. These data exhibit a threshold of approximately 1 eV and a maximum in the exchange cross section between 2 and 3 eV collision energy.

*Supported in part by AFOSR Contract F49620-80-C-0095 and in part by AFOSR Contract F49620-81-C-0022.

Published as Chapter 22 in Potential Energy Surfaces and Dynamics Calculations, D. G. Truhler, Ed., Plenum Press, New York, 1981.

APPENDIX B

SPHERICAL-HARMONIC EXPANSION TECHNIQUES
FOR MULTICENTER INTEGRALS OVER STO'S.

A REEXAMINATION FOR VECTOR PROCESSING COMPUTERS*

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ABSTRACT

In multicenter integral calculations, it is useful to express an atomic orbital as a spherical-harmonic expansion about a point displaced from the orbital's center. Through judicious choice of these expansion points, it is possible to calculate the general electron-repulsion integral for orbitals displaced at most by distances of the order of the bond lengths.

We have reexamined the utility of these orbital expansions for STO's in light of the availability of new computers with vector processing hardware. In particular, we have carried out studies for STO's typical of atoms through Ne. Impressive times have been achieved by new programs implemented on the CRAY-1 computer where the products of orbital l -expansions are essentially reduced to several multiplication cycle times. Convergence problems still remain for core-like STO's (large ζ 's) which suggests that a different approach should be implemented to handle this class of integrals.

*Supported in part by AFOSR Contract F49620-81-C-0097 and in part by AFOSR Contract F49620-81-C-0022.

Published as a chapter in ETO Multicenter Molecular Integrals, 1982, C. A. Weatherford, Ed., D. Reidel, Holland.

APPENDIX C

AB INITIO STUDY OF THE
ELECTRONIC STRUCTURE OF Li_2^-

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ABSTRACT

Calculations have been performed on the electronic structure and potential energy curves for the anion of Li_2 using CI wavefunctions optimized for the ground and excited molecular states connecting up to the $\text{Li } ^2\text{P}(2p) + \text{Li}^- ^1\text{S}(2p^2)$ dissociation limit. The ground $^2\Sigma_u^+$ state of Li_2^- lies entirely below the ground $X ^1\Sigma_g^+$ state of Li_2 and can therefore be treated using the standard variational treatment. The excited states of Li_2^- are, in general, unstable with respect to autoionization and are treated using the quasivariational stabilization method. We have located the position of the low-lying $^2\Sigma_g^+$ excited state of Li_2^- and have examined the possibilities for dissociative-attachment in this system. Our calculations predict an adiabatic electron affinity for Li_2 of 0.60 eV, in good agreement with previous studies. Comparisons of the excited electronic states with the H_2^- system indicate significant differences arising from the non-degenerate character of the Li atom excited states.

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To be published in Chemical Physics Letters, 1983.

APPENDIX D

DISSOCIATIVE-RECOMBINATION OF $e + H_3^+$.
AN ANALYSIS OF REACTION PRODUCT CHANNELS*

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ABSTRACT

Accurate ab initio calculations of the ground and excited H_3 hypersurfaces have been carried out within a configuration-interaction framework. These surfaces have been examined for geometries appropriate for an analysis of the reaction products of dissociative recombination of $e + H_3^+$. Direct recombination occurs through the 2A_1 resonance state which connects diabatically to $H_2^+ + H^-$. This resonance state is accessible for low-energy electron attachment to H_3^+ ions carrying three or more quanta of vibrational energy. Under these conditions the predicted products are $H^*(n=2) + H_2^+$ ($X\ ^1\Sigma_g^+$), where any excess vibrational energy in the H_3^+ ions is transferred to the product H_2 molecule. Direct dissociative recombination of H_3^+ ions in their ground vibrational state is unlikely for low collisional energies ($\lesssim 6$ eV) and indirect capture processes must be examined for this case.

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